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Sorption of Hydrophobic Organic Compounds by Sediments

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16. ABSTRACT

Thermodynamic and kinetic principles which govern the uptake of nonionic, hydrophobic organic chemicals by sediments in aqueous systems are summarized. Sorption onto organic-rich sediments can be modeled as a process where the hydrophobic compound partitions into the organic matter associated with the sediments analogous to the partitioning in the octanol water system resulting in a linear free energy relationship between the two partition coefficients. The influence of dissolved organic matter can be accounted for by considering a binding isotherm between the hydrophobic solute and dissolved macromolecules. In the case of mixed cosolvents, partition coefficients can be correlated with predictions based on the solvophobic model. Adsorption at the mineral-water interface becomes important when the adsorbate contains polar functional groups and/or when the adsorbate contains quite small concentrations of organic matter. Sorption can require more than a month to reach equilibrium for highly hydrophobic compounds, but can be adequately described by a radial diffusion model accompanied by the retarding influence of sorption.

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Sorption of Hydrophobic Organic Compounds by Sediments

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Thermodynamic and kinetic principles which govern the uptake of nonionic, hydrophobic organic chemicals by sediments in aqueous systems are summarized. Sorption onto organic-rich sediments can be modeled as a process where the hydrophobic compound partitions into the organic matter associated with the sediments analogous to the partitioning in the octanol water system resulting in a linear free energy relationship between the two partition coefficients. The influence of dissolved organic matter can be accounted for by considering a binding isotherm between the hydrophobic solute and dissolved macromolecules. In the case of mixed cosolvents, partition coefficients can be correlated with predictions based on the solvophobic model. Adsorption at the mineral-water interface becomes important when the adsorbate contains polar functional groups and/or when the adsorbate contains quite small concentrations of organic matter. Sorption can require more than a month to reach equilibrium for highly hydrophobic compounds, but can be adequately described by a radial diffusion model accompanied by the retarding influence of sorption.

Hydrophobic contaminants, such as halogenated hydrocarbons and polynuclear aromatic hydrocarbons are one of the most important classes of environmental pollutants. The hydrophobicity of these compounds is generally characterized by their physical properties, such as low aqueous solubility, high octanol/water partition coefficient, and high air/water partition coefficient (i.e., high Henry's constant). These properties vary over several orders of magnitude for the contaminants encountered in the ecosphere. Research on the sorptive interactions between sediments and hydrophobic organic solutes in aqueous solution has focused primarily on determining the solute and sediment properties that govern the sorption process. Information on such processes is necessary for modeling the environmental fate of these pollutants.

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Previous research has demonstrated that sorption of hydrophobic compounds by sediments can be estimated from (1) molecular parameters indicating the sorbate's hydrophobicity, such as octanol/water partition coefficient (K_{ow}), and (2) from the mass fraction of the organic carbon (f_{oc}) in the sorbent. The chemical principles of hydrophobic sorption by sediments have been reviewed most recently by Karickhoff (1). In general, the empirical relationship between sorption, K_{ow}, and f_{oc} has been developed using organic-rich sediments or soils, whereas relatively little attention has been given to low-organic, sandy aquifer materials. The purpose of this paper is to summarize the concepts of hydrophobic sorption and to address the limitations imposed by the influence of dissolved macromolecular material, sorption kinetics, the nonsingularity in the sorption and desorption isotherms and the conditions under which mineral surfaces influence sorption.

Adsorption Mechanisms

The mechanisms of adsorption of organic solutes--including hydrophobic, polar, and ionic species--onto surfaces have been summarized previously (2-5). Assuming that the various adsorptive mechanisms act independently, the free energy of adsorption (ΔG_{ads}) can be expressed as the sum of the individual contributions as follows (4):

$$\Delta G_{ads} = \sum \Delta G_i \qquad (1)$$

where ΔG_i corresponds to the free energy contributions of the possible adsorption mechanisms. The various mechanisms by which an organic solute may adsorb include (1) interactions between an organic ion and the electrical double layer, (2) ion exchange, including protonation followed by ion exchange, (3) coordination by surface metal cations, (4) ion-dipole interactions, (5) hydrogen bonding, and (6) hydrophobic interactions (2, 3). The first and second of these mechanisms are important only for ionizable compounds, which are not considered here. Coordination by exchanged and structural metal cations is important when the organic is a good electron donor (Lewis base) relative to water, such as amines (2). Similarly, the ion-dipole interactions between the charged surface and the uncharged adsorbate are also expected to be negligible in aqueous solution. Finally, because the carbon-hydrogen and the carbon-halogen bonds in halogenated hydrocarbons are only weakly acidic and basic, respectively (6), hydrogen bonding should account for only a small contribution to the total adsorption free energy. In addition, the relative insignificance of the hydrogen bond between a clay surface and an OH group of an adsorbed molecule has been demonstrated by IR spectroscopy (2).

The arguments presented above lead to the conclusion that the adsorption of nonionic compounds such as halogenated hydrocarbons results primarily from "hydrophobic bonding" or, perhaps more appropriately, the hydrophobic interaction (7). The thermodynamic driving force for hydrophobic interactions is the increase in entropy resulting from the removal, or decrease, in the amount of hydration water surrounding an organic solute in water. Studies have shown that the adsorption of aliphatic amines onto clays (8) and surfactants onto oxides (9) increased linearly with increasing hydrocarbon chain length, with each additional methylene group contributing approximately -1.8 to -2.5 kJ/mol to the total free energy of adsorption. These values are slightly less negative than the -2.9 to -3.7 kJ/mol observed for the transfer of a methylene group in a hydrocarbon chain from an aqueous phase to an organic solvent (10, 11). The dependence of the adsorption intensity on the chain length indicates that hydrophobic interactions are responsible for the increased adsorption for the longer chain lengths.

In considering the sorption of nonionic solutes onto sediments, it is generally found that the sorption isotherm for hydrophobic organic solutes are approximately linear over a substantial concentration range and can be adequately described by a constant distribution coefficient, K_d (1). K_d tends to be variable over several orders of magnitude for a given solute with different solids, but it generally correlates with the organic carbon content of the sediment. By attributing all the sorption to the organic matter, an organic carbon partition coefficient, K_{oc}, can be defined by

$$K_{oc} = \frac{K_d}{f_{oc}} \qquad (2)$$

where f_{oc} is the mass fraction of organic carbon of the sorbent. K_{oc} generally varies only by factors of three to five for a given solute (12). K_{oc} typically correlates well with physico-chemical properties of the sorbate, such as aqueous solubility (S) or the octanol-water partition coefficient (K_{ow}), again suggesting that hydrophobic interaction predominates. The correlation of K_{oc} with K_{ow} has led to the definition of linear free-energy relationships (LFER) of the form

$$\log K_{oc} = a \log K_{ow} + b \qquad (3)$$

or,

$$\log K_{oc} = c \log S + d \qquad (4)$$

where a, b, c, and d are constants resulting from a regression analysis. K_{ow} is most widely used for correlations with K_{oc} because of the availability of an extensive data base and estimation methods (9, 11). Other correlations have been proposed, most notably with the aqueous solubility, S, (14-16).

In addition to the dependence of sorption on the organic fraction of the sorbent, and the K_{ow} of the sorbate, Chiou et al. (13) cite the following observations as support for the hypothesis that the sorptive mechanism is hydrophobic partitioning into the organic (humic) fraction of the sediments: (1) the linearity of the isotherms as the concentration approaches solubility, (2) the small effect of temperature on sorption, and (3) the lack of competition between sorbates for the sorbent. These arguments also illustrate the applicability of the K_d approach for modeling sorption on hydrophobic compounds; an approach which has been criticized when used in the context of adsorption of trace metals onto oxides (17).

Partitioning Thermodynamics

The LFER that results when correlating partitioning in the octanol-water system and the humic substances-water system implies that the thermodynamics of these two systems are related. Hence, much can be learned about humic substances-water partitioning by first considering partitioning in the simpler octanol-water system. The thermodynamic derivation that follows is based largely on the approach developed by Chiou and coworkers (18-20), Miller et al. (21), and of Karickhoff (1, 22). In the subsequent discussion, we will adopt the pure liquid as the standard state and, therefore, use the Lewis-Randall convention for activity coefficients, i.e., $\gamma = 1$ if the mole fraction $x = 1$.

Partitioning in Octanol-Water Systems. At equilibrium, the chemical potential of a solute (defined as $\mu_i = \mu_i^\circ + RT \ln \gamma_i x_i$) is equal in the octanol and the water phase. Hence, we may write

$$\gamma_w^* x_w^* = \gamma_o^* x_o^* \tag{5}$$

where γ_w^* and γ_o^* are the activity coefficients of the solute in the aqueous phase and the octanol phase, respectively, and x_w^* and x_o^* are the mole fractions of the solute in the water and the octanol phases, respectively. The asterisks denote that the two phases are not pure but are saturated with the other "immiscible" solvent. In dilute solutions, the mole fractions x can be approximated by $x = C \cdot V_s$, where C is the molar concentration and V_s is the molar volume of the solvent. Hence we can write Equation 5 in terms of the molar concentrations and obtain an expression for the octanol/water partition coefficient, $K_{ow} = C_o/C_w$ in terms of the activity coefficient and the molar volumes of octanol and water (19):

$$K_{ow} = \frac{\gamma_w^*}{\gamma_o^*} \frac{V_w^*}{V_o^*} \tag{6}$$

where V_w^* and V_o^* are the molar volumes of the water saturated with octanol and the octanol saturated with water, respectively. The asterisks in Equation 6 denote that the phases are not pure but in fact are saturated with the other "immiscible" solvent.

We may consider the aqueous solubility as partitioning of a compound between its pure state in liquid form and the saturated aqueous phase. Then the partitioning coefficient (Equation 6) may be written as

$$S = \frac{1}{V_w^* \gamma_w^*} \tag{7}$$

where the asterisks have been omitted since the cosolvent (octanol) is absent and the organic compound is assumed to be a pure liquid ($x_o = 1$), which in turn implies that the organic solute is at the standard state or $\gamma_o = 1$ (23).

A correction to Equation 7 is required for organic solutes that are solids at the temperature and pressure of the partitioning system. This correction is required, because the intermolecular forces in the crystal must be overcome before the chemical enters solution. However, it cancels out in octanol/water systems, since the correction applies to both phases equally (23). One method that accounts for the crystalline energy effect is to use an estimate of the solubility of the supercooled liquid given by (24):

$$\log S_\ell = \log S_s + \frac{\Delta S_f}{2.303R} \left(\frac{T_m - T}{T} \right) \tag{8}$$

where S_ℓ and S_s are the molar solubilities of supercooled liquid and the solid, respectively, ΔS_f is the entropy of fusion, T_m and T are the melting temperature and the temperature of interest, and R is the gas constant. Since the entropy of fusion is positive for nonionic organic compounds (24), the solubility of the supercooled liquid is larger than the solubility of the solid as shown by Equation 8. The subsequent discussion assumes that the solubility of a solid organic solute is expressed as the solubility of the supercooled liquid.

Since the solubility of octanol in water is only 0.0045M (9), the molar volume of the aqueous phase saturated with pure octanol can be approximated by the molar volume of pure water ($V_w^* = V_w$). With this approximation, Equations 6 and 7 give

$$K_{ow} = \frac{1}{SV_o^*} \frac{\gamma_w^*}{\gamma_w \gamma_o^*} \tag{9}$$

which can be rewritten as

$$\log K_{ow} = -\log SV_o^* + \log \frac{\gamma_w^*}{\gamma_w} - \log \gamma_o^* \tag{10}$$

If an ideal solution is formed in the octanol phase, and the solute in the aqueous phase is not affected by the dissolved octanol, then the last two factors in Equation 10 equal zero. Under these assumptions, an ideal octanol/water partition coefficient (K_{ow}°) can be defined by (19):

$$\log K_{ow}^\circ = -\log S - \log V_o^* \tag{11}$$

Equation 11 implies that under these idealized conditions a log-log plot of S versus K_{ow} will have a slope of -1 and an intercept of $-\log V_o^*$ (19). The factors γ_w^*/γ_w and $1/\gamma_o^*$ can be viewed as corrections for the activity change in the aqueous phase caused by the octanol dissolved in the water, and for nonideality in the octanol caused by the incompatibility of the solute with water-saturated octanol, respectively.

Nonidealities in Water-Saturated Octanol. Chiou et al. (19), Tewari et al. (25) and Banerjee et al. (26) presented solubility data and octanol/water partition coefficients for 125 organic solutes. Figure 1 shows data from these three sources, the least-squares

regression line for all of the data, and the ideal line as defined by Chiou et al. (19). The regression line has a slope of -0.860 and differs from the ideal slope of -1 at the 99.5% significance level. These deviations are caused by either (1) a linear increase in $\log \gamma_o^*$ with decreasing log S, (2) a linear decrease in $\log \gamma_w^*/\gamma_w$ with increasing log S, or (3) a combination of both. Chiou et al. (19) reported that both factors were significant: the solubility of the hydrophobic compounds hexachlorobenzene ($\log K_{ow} = 5.50$) and DDT ($\log K_{ow} = 6.36$) were enhanced by dissolved octanol to the extent of 80% and 160%, respectively, such that $\log(\gamma_w^*/\gamma_w)$ accounted for approximately one-third of the deviation from the ideal line. In contrast, Miller et al. (21) observed that γ_w^* and γ_w were indistinguishable for compounds with $\log K_{ow}$ up to 5.8. Calculations based on the solvophobic model (27), discussed below, suggest a negligible effect of dissolved octanol on the solubility of pyrene in water ($\log K_{ow} = 5.18$). Therefore, it appears that the variation in $\log \gamma_o^*$ accounts for the majority of the deviations from the ideal line.

If all of the deviations between the ideal line (Equation 11) and the observed data are attributed to $\log \gamma_o^*$, the empirical correlation between log S and $\log K_{ow}$ (Figure 1) can be combined with Equation 9 to give:

$$\log \gamma_o^* = 0.16 \log K_{ow} + 0.08 \qquad (12)$$

Equation 12 shows that γ_o^* increases by a factor of only 7 as K_{ow} increases by 10^5.

The most important factor in determining K_{ow} is the aqueous-phase activity coefficient (aqueous solubility) of the organic solute. The observed partition coefficients are less than the ideal partition coefficients (K_{ow}^o) as result from 1) the incompatibility of the solute in water-saturated octanol and, to a lesser degree, 2) the depression of the aqueous-phase activity coefficient by octanol. The values of $\log \gamma_o^*$ and $\log \gamma_w^*/\gamma_w$ increase linearly with decreasing log S.

Partitioning in Natural Organic Matter-Water Systems. For K_{oc} we may write, by analogy to Equation 6,

$$K_{oc} = \frac{\gamma_{w/oc}^* V_w^*}{\gamma_{oc/w}^* V_{oc}^*} \cdot \frac{1}{\rho_{oc}} \qquad (13)$$

where $\gamma_{w/oc}^*$ is the activity coefficient of the solute in water saturated with dissolved organic carbon derived from humic substances and $\gamma_{oc/w}^*$ is the activity coefficient in humic substances saturated with water. This analogy is justifiable since sorption to organic matter proceeds by a process similar to hydrophobic liquid-liquid partitioning (1, 13, 15, 20). The density of the organic carbon phase is included in Equation 12 so that K_{oc} is expressed in the conventional units of cm^3/g. By multiplying the numerator and denominator of Equation 13 by $V_o^* \gamma_w^* \gamma_o^*$, substituting K_{ow} as defined in Equation 6, and assuming $\gamma_w^* = \gamma_w$ as before, it can be shown that

$$K_{oc} = C_1 K_{ow} \left(\frac{\gamma_o^*}{\gamma_{oc/w}^*}\right)\left(\frac{\gamma_{w/oc}^*}{\gamma_w}\right) \qquad (14)$$

The quotient $V_o^*/V_{oc}^* \rho_{oc}^*$ has been substituted by C_1, since this quantity should be constant for a given sorbent. Equation 14 illustrates that K_{oc} is proportional to K_{ow} but is modified by two terms, $(\gamma_o^*/\gamma_{oc/w}^*)$ and $(\gamma_{w/oc}^*/\gamma_w)$, which account for the differences in activity coefficients in the aqueous and organic phases, respectively. In the following discussion, we examine the factors that influence the activity coefficients in the organic phases $(\gamma_o^*/\gamma_{oc/w}^*)$ and the activity coefficients in the aqueous phase $(\gamma_{w/oc}^*/\gamma_w)$.

Sorption data from several different studies are correlated with K_{ow} in Figure 2. The data presented include halogenated aliphatics and aromatics, alkyl-substituted aromatics, and polynuclear aromatic hydrocarbons. By selecting data for these classes of compounds, we have minimized possible influences of complexation, hydrogen bonding, strong dipole interactions, and charge effects. Therefore the correlation indicated in Figure 2 represents hydrophobic partitioning into the organic matter and water. In view of Equation 14, the observed slope of less than unity must arise from a negative linear dependence of $\log(\gamma_o^*/\gamma_{oc/w}^*)(\gamma_{w/oc}^*/\gamma_w)$ on $\log K_{ow}$. In the subsequent discussion, we examine this dependence, which defines the coefficient a of Equation 3.

Nonidealities in Humic Polymers

Organic-Phase Nondealities. To assess the impact of nonideality in the organic matter, we assume for illustrative purposes that $\gamma_{w/oc}^*/\gamma_w^*$ equals unity. Consequently, Equation 14 simplifies to

$$K_{oc} = C_1 K_{ow} \frac{\gamma_o^*}{\gamma_{oc/w}^*} \qquad (15)$$

Substituting the previously derived expression for γ_o^* (Equation 12) gives

$$K_{oc} = C_2 K_{ow}^{1.16} \frac{1}{\gamma_{oc/w}^*} \qquad (16)$$

where C_2 equals $C_1 \times 10^{0.08}$. This substitution yields an expression of K_{oc} as a function of the molecular property K_{ow} and the activity coefficient of the solute in the water-saturated organic matter. Equivalently, K_{oc} could be expressed as a function of the solubility of the solute in water by substituting K_{ow} with $1/S^{0.84}$ (see Figure 1).

In logarithmic form, Equation 16 rearranges to

$$\log K_{oc} = 1.16 \log K_{ow} + \log C_2 - \log \gamma_{oc/w}^* \qquad (17)$$

To account for the experimentally observed slope of 0.92 (Figure 2), $\gamma_{oc/w}^*$ must be positively correlated with K_{ow} if C_2 is a constant; otherwise the slope of the correlation would equal 1.16.

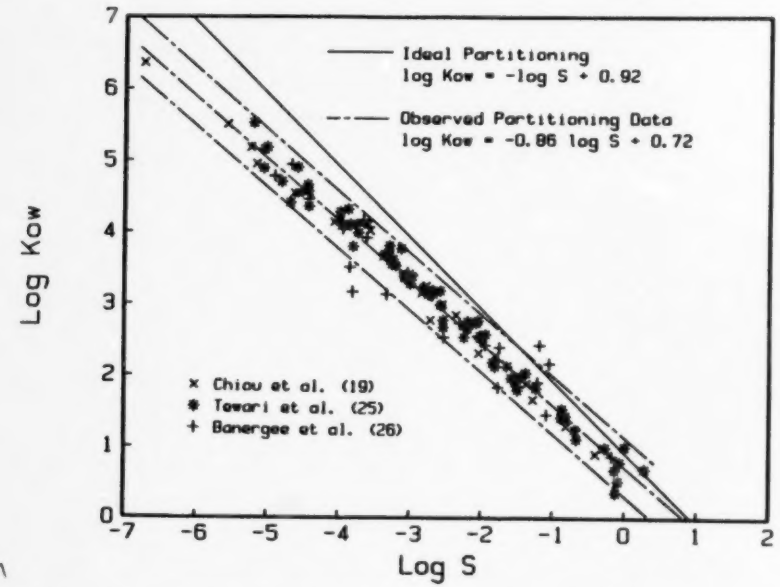
Ideal Partitioning
log Kow = -log S + 0.92
Observed Partitioning Data
log Kow = -0.86 log S + 0.72
x Chiou et al. (19)
* Tewari et al. (25)
+ Banerjee et al. (26)
Log Kow
Log S

Figure 1. The relationship between the aqueous solubility and octanol-water partition coefficient for nonpolar organic solutes.

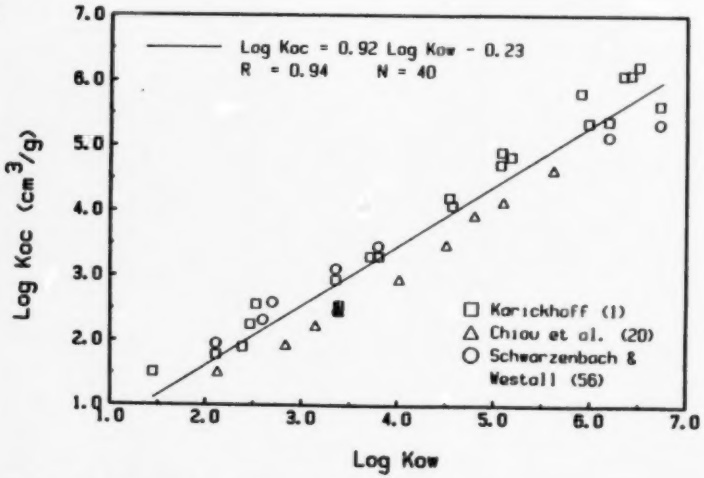

Figure 2. The correlation between the organic carbon partition coefficient and the octanol water partition coefficient.

It is well known in polymer science that a small amount of organic solvent dissolved in a polymer results in large negative deviations from Raoult's law because of the large entropic effects without the associated enthalpic effects (28). This is a consequence of the mixing of molecules of greatly different sizes (29). Therefore, it is unreasonable to assume an activity coefficient equal to one in the organic phase. Chiou et al. (20) have treated the humic material as a non-swelling amorphous polymer and used the Flory-Huggins theory to estimate the activity ($x_o^* \gamma_o^*$) of a solute partitioned into the humic matter from (28, 30)

$$\ln x_o^* \gamma_o^* = \ln \phi + \phi_p\left(1 - \frac{\bar{V}}{\bar{V}_p}\right) + \chi\phi_p^2 \qquad (18)$$

where ϕ and ϕ_p are the volume fractions of the solute and humic phase, respectively, $\bar{V}$ and $\bar{V}_p$ are the molar volume of the solute and an estimated average molar volume of the humic polymers, respectively. The Flory-Huggins interaction parameter (χ) characterizes the interaction energy between a solute molecule and the polymer.

With the assumption of a dilute solution in the humic phase (i.e., $\phi_p \approx 1$, $\bar{V} \ll \bar{V}_p$, and $\phi = n_1\bar{V}/n_2\bar{V}_p$, Equation 18 simplifies to

$$\ln \gamma_{oc/w}^* = \ln(\bar{V}/\bar{V}_p)) + \chi + 1 \qquad (19)$$

Equation 19 illustrates that $\ln \gamma_{oc/w}^*$ (or $\log \gamma_{oc/w}^*$) will be less than zero for $\bar{V} \ll \bar{V}_p$ and small χ. Under these conditions, the large disparity in molecular size favors partitioning to the humic material relative to organic solvent phases with smaller $\bar{V}$.

The Flory-Huggins interaction parameter, χ, is the sum of enthalpic (χ_H) and entropic (χ_S) contributions to the polymer-solute interactions (28). χ_S is an empirical constant related to the coordination of the polymer subunits (29). Chiou et al. (20) have selected a value of 0.25 for χ_S of humic matter. From regular solution theory, χ_H is given by

$$\chi_H = \frac{\bar{V}}{RT}(\delta - \delta_p)^2 \qquad (20)$$

where δ and δ_p are the solubility parameters of the solute and humic material, respectively (29).

For a constant V_p and χ_s, Equations 17, 19, and 20 can be combined to give

$$\log K_{oc} = 1.16 \log K_{ow} - \log \bar{V} - \frac{\bar{V}}{RT}(\delta - \delta_p)^2 + C_3 \qquad (21)$$

This equation illustrates that K_{oc} depends on the solute parameters K_{ow}, V, and δ. Since molar volume and $\log K_{ow}$ are positively correlated ($\log K_{ow} = 0.49 + 0.020V$; 21), K_{oc} could be expressed as a function of the solute parameters K_{ow} and δ, and polymer parameter δ_p.

Table I presents an evaluation of Equation 21 based on previously reported values for $\log K_{ow}$, V, and δ. The constant C_3 was calculated from the $\log K_{oc}$ of benzene estimated from Figure 2. Estimates of $\log K_{oc}$ for the remaining compounds in Table I are presented for δ_p equal to 10.3 and 11.5. The value of 10.3 corresponds to the δ_p implied from solvent extraction studies (31). In this case,

Table I. K_{oc} Estimated from K_{ow}, $\bar{V}$, δ, and δ_p

Compound	log K_{ow}*	$\bar{V}$* (cm^3/mol)	δ† (cal/cm^3)$^{1/2}$	log K_{oc}	
				δ_p = 10.3	δ_p = 11.5
benzene	2.13	88.7	9.2	1.51	1.51
trichloroethylene	2.53	89.0	9.2	1.96	1.96
toluene	2.65	106.3	8.9	1.83	1.55
chlorobenzene	2.98	116.9	9.5	2.42	2.36
ethylbenzene	3.13	122.5	8.8	2.19	1.71
m-xylene	3.20	123.2	8.8	2.27	1.78
naphthalene	3.33	148.0	9.9	2.84	2.85
1,2-dichlorobenzene	3.38	137.8	10.0	2.92	3.04
propyl benzene	3.69	139.4	8.6	2.54	1.77
phenanthrene	4.54	197.0	9.9	4.05	3.84
anthracene	4.57	199.0	9.8	4.05	3.74
			slope	1.04	0.92
			intercept	-0.82	-0.60
			R^2	0.92	0.70

* Ref. 21. † Ref. 32.

the estimated log K_{oc} values do correlate well with log K_{ow}. The slope of the correlation (1.04) is less than 1.16 and closer to observed data. A close match of the experimental and estimated slope is obtained with δ_p = 11.5. If δ_p = 11.5, which is approximately equal to the average of previously suggested values (20, 31), then the slope from the estimated log K_{oc} values is nearly identical to that presented in Figure 2. However, the correlation coefficient decreased markedly to 0.70. This decrease in r^2 may be due to the limited applicability of the Flory-Huggins theory to hydrophobic partitioning into sediment organic matter, which may not exhibit ideal polymer properties, as assumed by Flory-Huggins. Although more complex thermodynamic models have been proposed (30), their use is unwarranted at this time given that solubility parameters for the humic material are not well known and that numerous assumptions were required in deriving Equation 21. Nevertheless, the calculations based on the Flory-Huggins theory are encouraging in that the trends predicted in terms of the LFER slope do agree with observed data.

Aqueous-Phase Nonidealities

The Effect of Dissolved Humic Material. Several investigators have reported that the solubilities of strongly hydrophobic solutes increase in the presence of dissolved organic matter (DOC) (33-38). This solubilization phenomenon is most likely a consequence of the solute binding to dissolved macromolecules (39). Such binding may alter rates of photolysis, hydrolysis, volatilization, or biodegradation, all of which can affect the environmental fate of trace organic solutes (40). In the context of this work, the most important effect of binding is a lowering of the thermodynamic activity

of the solute when compared with the activity in the absence of the macromolecule (39). By analogy to Equation 7, we may express S_T, the total solubility of a solute in the presence of dissolved humic material, as

$$S_T = \frac{1}{\bar{V}_w \gamma^*_{w/oc}} \tag{22}$$

where $\gamma^*_{w/oc}$ is the activity coefficient of the solute in water in the presence of humics. It is therefore clear that the reported solubilization phenomenon is directly related to changes in $\gamma^*_{w/oc}$.

Chiou et al. (41) proposed that a linear equilibrium model may be used to describe the effect of DOC on the solubility of an organic solute. The model regards a hydrophobic solute in solution as being either "free" or truly dissolved, on the one hand, or "bound" or complexed with the humic material on the other hand. The model relates the free and DOC-bound concentrations, C_w and C_b respectively, by a simple partitioning equilibrium constant

$$C_b = C_w C_{doc} K_{doc} \tag{23}$$

where C_{doc} is the concentration of the DOC and K_{doc} is the DOC-water distribution coefficient (41, 42). The total measured concentration C_T of organic solute in solution is merely the sum of C_w and C_b which is given by

$$C_T = C_w(1 + C_{doc}K_{doc}) \tag{24}$$

The value of K_{doc} is presently uncertain, but recent studies report that K_{doc} varies with the source of the humic material, the solution pH, and the ionic strength (42, 43). As an approximation, K_{doc} can be estimated from K_{oc}, using one of the correlations developed between K_{ow} and K_{oc}. Alternatively, as an upper bound, K_{doc} may be assumed equal to the K_{ow} of the compound (1).

Equation 24 may be used to predict the effect of DOC on the total solubility of a hydrophobic compound in the presence of DOC (S_T) as a function of S and the above binding model. At solubility ($C_T = S_T$), the ratio S/S_T is equal to $\gamma^*_{w/oc}/\gamma_w$ (Equations 7 and 22), and therefore, by considering Equation 24 we may write:

$$\frac{\gamma^*_{w/oc}}{\gamma_w} = (1 + C_{doc}K_{doc})^{-1} \tag{25}$$

where the assumption of constant molar volume and dilute solution have been made.

By analogy to Equations 10 and 11 we may express the observed partition coefficient K_{oc} as

$$K_{oc} = K^\circ_{oc} \frac{\gamma^*_{w/oc}}{\gamma_w} \tag{26}$$

where K°_{oc} is an ideal partition coefficient, which applies only when DOC has no effect on the dissolved solute ($\gamma^*_{w/oc} = \gamma_w$). As discussed previously, $\gamma^*_{w/oc}/\gamma_w$ is the correction factor which accounts for the

solubilizing effect of DOC. Combining Equations 25 and 26 results in

$$K_{oc} = K_{oc}^{o}(1 + C_{doc}K_{doc})^{-1} \quad (27)$$

This equation, which is identical to equation 9 of Gschwend and Wu (44), allows one to estimate the effect of DOC on the observed partition coefficients. If we assume that K_{doc} can be related to K_{ow} by a LFER ($\log K_{doc} = a \log K_{ow} + b$), we obtain

$$\frac{\gamma_{w/oc}^{*}}{\gamma_{w}} = \left(1 + C_{doc}\, a\, K_{ow}^{b}\right)^{-1} \quad (28)$$

where a and b are empirical constants. Figure 3 shows $\gamma_{w/oc}^{*}/\gamma_{w}$ as a function of K_{ow} at various DOC concentrations, using the correlations between K_{ow} and K_{oc} reported by Karickhoff et al. (15). These model calculations show that at DOC concentrations representative of natural systems, (e.g., $C_{doc} < 50$ mg/l), binding of organic solutes to DOC should be insignificant for compounds with $\log K_{ow} < 4$. For a compound with $\log K_{ow}$ equal to 6.0 and a C_{doc} equal to 10 mg/l, however, the apparent partitioning coefficient is approximately an order of magnitude smaller than the ideal value. These predictions have been supported by experimental solubility data showing that moderately hydrophobic compounds such as toluene (44) and lindane (45) are not influenced by DOC, whereas DOC markedly affects highly hydrophobic compounds such as DDT (42), PCB (46) and polynuclear aromatic hydrocarbons (47).

Calculations which consider binding of sorbing solutes to dissolved humic matter show that the previously reported inverse relationship between effect of sediment concentration and sorption equilibrium can be accounted for by desorption of humic material followed by binding to the DOC (46, 48).

One of the important assumptions made in deriving Equations 24 through 28 is that K_{doc} is independent of C_{doc}. However, it has been observed that K_{doc} is inversely related to C_{doc} (42, 43, 45, 47) in a manner that is analogous to the sediment concentration effect on K_{oc}, although the dependence is substantially weaker. Thus, questions still remain regarding the cause of the sorbent concentration effect, since the binding of solutes to macromolecules, which was used to interpret the effect of sorbent concentration, also varies with loading of sorbent sites.

Influence of Organic Cosolvents. Rao et al. (49) have recently presented a solvophobic model for estimating the sorption of a hydrophobic solute from a mixed solvent. This model is based on the work of Yalkowsky et al. (27), who developed an empirical relationship between the solubility in a mixed solvent system, S_m, and that in pure water given by

$$\ln S_m = \ln S + \sigma_c f_c \quad (29)$$

where f_c is the volume fraction of cosolvent. For hydrophobic solutes, the parameter σ_c is given from empirical relationships by

$$\sigma_c = \frac{\Delta\gamma^{c}(HSA)}{kT} \quad (30)$$

where $\Delta\gamma^{c}$ is the difference in surface tension of pure water and pure cosolvent, HSA is the hydrophobic surface area of the solute, k is the Boltzmann constant, and T is the absolute temperature. Based on the inverse relationship between K_{oc} and S (Equation 4), the following relationship can be derived (49, 50):

$$\ln(K_{oc}^{m}/K_{oc}^{w}) = -\alpha\, \sigma_c f_c \quad (31)$$

where the superscripts m and w denote the mixed solvent and water, respectively, and α is an empirical constant. Equation 31 predicts that (1) K_{oc}^{m} should decrease exponentially with increasing f_c for a given solute and (2) the decrease in K_{oc}^{m} caused by a given solvent should be greatest for the least soluble (largest HSA) compounds. These predictions have been verified experimentally for water-methanol, and water-acetone cosolvent systems (50, 51).

Typically, K_{oc} is expressed in units of volume of solution per mass of organic carbon. Fu and Luthy (50) observed that a plot of $\ln(K_{oc}^{m}/K_{oc}^{w})$ versus f_c was nonlinear when K_{oc} was expressed in the common units of volume per mass of organic carbon. A linear plot was obtained when K_{oc} was expressed in units of moles of solvent per gram of organic carbon.

Using values of σ_c determined from solubility measurements, Fu and Luthy (50) found an average value of α equal to 0.51, which shows that the decrease in K_{oc}^{m} was half of that expected from the increase in solubility. This was interpreted as evidence that the cosolvent was swelling the organic fraction of the soil and consequently increasing the accessibility to the organic matter (50) in accordance with the gel-partition model (31).

Frequently it is convenient, when conducting sorption experiments, to use a cosolvent such as methanol to facilitate transfer of a volatile or insoluble solute. Equation 31 may be used to estimate the effect of the cosolvent on measured sorption coefficient. If f_c equals 10^{-3} and α is conservatively chosen as unity, the methanol is predicted to decrease the sorption of anthracene ($\sigma_c = 9.76$; $\log K_{ow} = 4.54$; 50) by 1% relative to the case of no cosolvent. The effect of the cosolvent should be smaller for solutes with smaller HSA (or K_{ow}), which is consistent with the observed negligible impact of methanol at $f_c \leq 10^{-3}$ on the sorption of hexachloroethane ($\log K_{ow} = 3.6$; 52).

Limitations of Partitioning Theory

Inefficiency of Partitioning. Equations 2-4 imply that the sorptive capacity (K_{oc}) of organic matter for hydrophobic organic solutes is independent of origin and of the composition of the mineral matrix. However, investigators studying individual particle size fractions found that the organic matter associated with a coarse or sand fraction is apparently less efficient in sorbing organics than that associated with the finer materials (15, 53). To account for the relative inefficiency of the f_{oc} of the sand fraction, Equation 2 may be rewritten as

$$K_{oc} = \frac{K_d}{\Omega f_{oc}} \quad (32)$$

where Ω is an efficiency factor similar to that originally defined by Lambert (54), which always equals unity with the exception of sandy soils, for which Ω would be less than unity. Either kinetic limitations or fundamentally different properties of the organic matter associated with the coarse grain fraction could account for the inefficiency factor.

Adsorption on Inorganic Surfaces. McCarty et al. (55) and Karickhoff (1) proposed a two-phase model for sorption onto mineral surfaces and organic matter partitioning. This model hypothesizes that sorption to inorganic surfaces may occur simultaneously with the accepted partitioning into the organic matter. Assuming additivity of these two contributions, K_d can be estimated from

$$K_d = f_{oc}K_{oc} + f_{io}K_{io} \quad (33)$$

where f_{io} and K_{io} are the fraction and the distribution coefficient for the inorganic material, while f_{oc} and K_{oc} are as previously defined. If only the organic and one inorganic phase is considered, the sum of f_{io} and f_{oc} equals one. For a given mineral, K_{io} is hypothesized to be the product of the specific surface area, S_A, and a specific surface adsorption constant, K_s. Therefore, the overall distribution coefficient can be given by

$$K_d = f_{oc}K_{oc} + f_{io}S_AK_s \quad (34)$$

The inorganic contribution, K_{io}, for chromatography-grade silica was found to depend weakly on K_{ow} ($\log K_s = 0.16\ K_{ow}$) (55), which is consistent with the results for silica and alumina obtained by Schwarzenbach and Westall (56).

Figure 4 presents distribution coefficients predicted from the two-phase model for two values of f_{oc} and S_A. Figure 4 shows that the dominance of one or the other contribution to sorption depends on two factors: K_{ow} and f_{oc}. For a given f_{oc}, compounds with low K_{ow} are influenced primarily by K_{io}, while compounds with higher K_{ow} are influenced primarily by K_{oc}. Alternatively, at a given K_{ow} and S_A, the model predicts the dominance of inorganic adsorption below a certain f_{oc} and dominance of organic-phase partitioning above this f_{oc}. The range of organic and inorganic sorption dominance depends on both the K_{ow} and the S_A.

The two-phase model proposed by McCarty et al. (55) is based in part on the assumption of independently acting organic and inorganic sorption sites. Shin et al. (57) and Pierce et al. (58) reported that the distribution coefficient for sorption of DDT increased after the oxidation or removal of some of the organic matter from the sorbent. Karickhoff (1) has interpreted this increase as evidence that the humic material had blocked clay sorption sites. Conversely, Chiou et al. (41) proposed that the oxidation process may have preferentially removed soluble organics which, if present in the aqueous phase, would decrease the sorption intensity due to binding of the organic solute to the DOC. This difference emphasizes the need for characterizing the sorption properties of the dissolved as well as sorbed organic matter and of the mineral matrix.

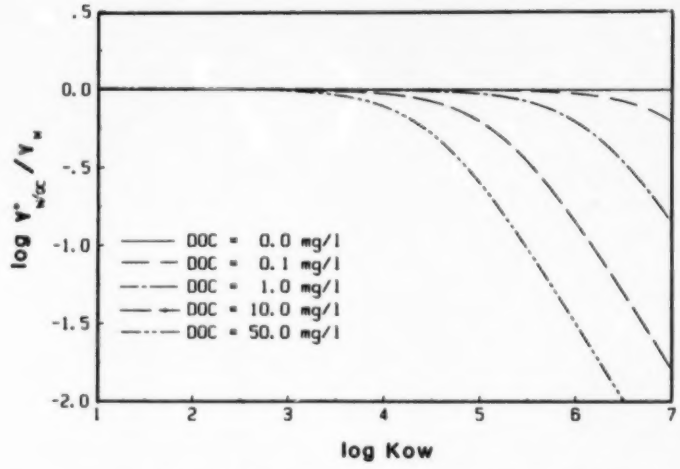

Figure 3. The effect of dissolved organic carbon on the aqueous activity coefficient estimated from the octanol-water partition coefficient.

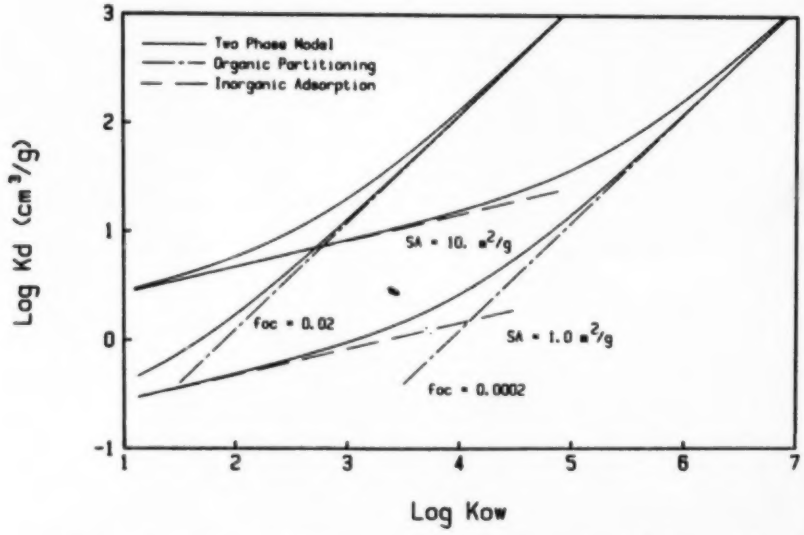

Figure 4. Distribution coefficients predicted from the two-phase sorption model.

Karickhoff (1) presented data that show more sorption than can be explained by simple partitioning theory when the expanding clay matter to organic matter ratio (cm:om) is "high". The term high is a relative term that cannot be easily quantified, but appears to be inversely related to K_{ow}, as predicted by the two-phase model. For the nitrogen heterocycles simazine (log K_{ow} = 2.16) and biquinoline (log K_{ow} = 4.31), the limiting cm:om ratio is 30:1. Pyrene, which is more hydrophobic (log K_{ow} = 5.18) and contains no polar moieties unlike the previous two compounds, was not strongly influenced by the clays. Similar data have been observed for sorption of amino- and carboxy-substituted polynuclear aromatic hydrocarbons (59), acetophenone (60), and α-naphthol (61).

The data from these various sources are presented in Figure 5 along with partitioning data previously presented in Figure 2. The partitioning data for the polar solutes are in agreement with general predictions of the two-phase model; specifically, the deviations are greatest for the least hydrophobic compounds. All of these compounds exhibit larger K_{oc} values than predicted from the organic matter partitioning theory, probably because of the presence of polar moieties which can participate in nonhydrophobic bonding, such as complexation of exchanged cations by the amino or carboxyl groups (2), hydrogen bonding (1), and even covalent bonding (62).

Organic compounds containing polar functional groups are not the only organic solutes that can participate in sorption interactions in excess of organic matter partitioning. Schwarzenbach and Westall (56) found that silicon and aluminum oxides, non-expanding clay minerals, and a low f_{oc} aquifer material, all exhibited more sorption capacity for halogenated and aromatic solutes than could be explained by partitioning into the organic matter. Furthermore, all of these samples with this "anomalously" high sorption capacity had f_{oc} values less than 0.001, which led them to caution against using any of the numerous correlations when the sorbent has an f_{oc} below 0.001.

In support of this finding, Curtis et al. (63) found enhanced sorption for five halogenated organic solutes onto an aquifer material with both a low surface area (0.8 m^2/g) and a low f_{oc} (0.0002). These data, along with those of Schwarzenbach and Westall (56) are presented in Figure 6 along with the partitioning data presented in Figure 2. Unlike the data presented in Figure 5, all of the data presented in Figure 6 are for halogenated aliphatic and aromatic compounds, and hence specific sorption mechanisms, such as complexation interactions or hydrogen bonding, should be negligible. The higher than predicted K_{oc} values for the sorbents with low f_{oc} suggest that sorption onto the mineral surfaces is a significant factor. The partition constant correlates positively with K_{ow}, which is expected, since both the free energy of sorption and partitioning in octanol/water increase linearly with the number of methylene groups (8-11).

Since adsorption at a mineral surface is a replacement process, we would expect mineral surfaces with weak affinity for water to have the strongest affinity for hydrophobic solutes. Infrared spectroscopy shows that siloxane surfaces on clays with little isomorphic substitution form weaker hydrogen bonds than water forms with itself (64), which corresponds to one of the definitions of a hydrophobic surface offered by Texter et al. (65). Therefore,

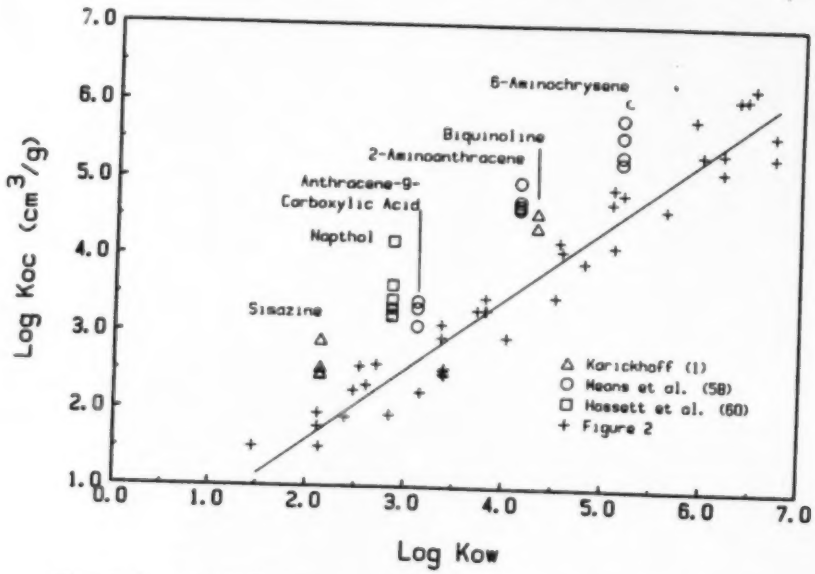

Figure 5. The influence of mineral surfaces on the sorption of organic solutes containing polar functional groups.

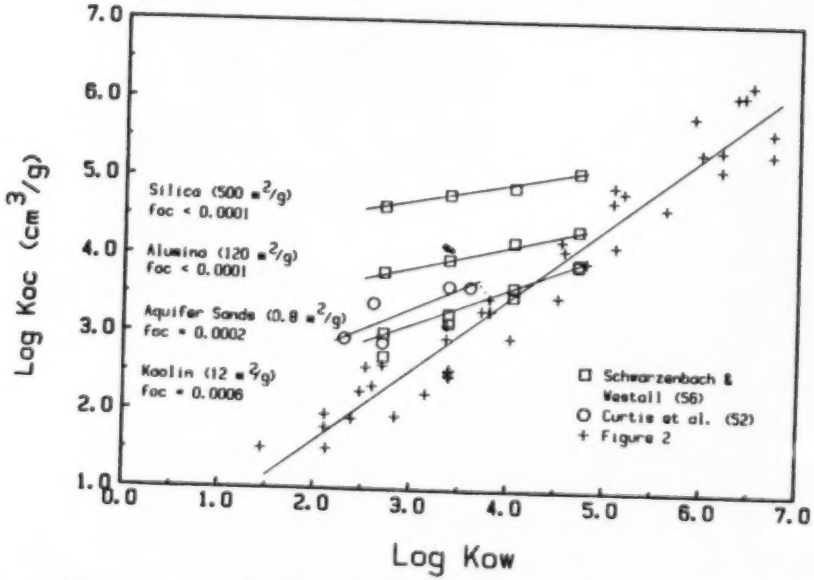

Figure 6. The influence of mineral surfaces on the sorption of organic solutes containing no functional groups.

mineral surfaces of sediments need to be characterized with respect to their affinity for water in order to predict adsorption of hydrophobic solutes.

Sorption Kinetics

The rate at which pollutants sorb to sediments has frequently been assumed to occur rapidly and consequently equilibration studies have often been conducted by mixing sample for 24 hours. Karickhoff (1, 66) has reported that sorption may require up to two months to reach an apparent equilibrium. Similarly, desorption has also been observed to require on the order of months to reach completion (67, 68). McCall and Agin (67) observed that the desorption rate of picloram was inversely related to the contact time.

Two models, a first-order kinetic model and a hindered diffusion model, have been proposed to describe the sorption and desorption rates of hydrophobic molecules. The possible origin of slow sorption rates include (1) the hindering of diffusion by the polymer-like organic macromolecules (31), and (2) diffusion in microporous minerals or into the interlamellar regions of expanding clays. These two processes may interact synergistically in the case of carbonate minerals, which can be both porous and contain significant amounts of organic carbon (69).

The First-Order Kinetic Model. Karickhoff (1, 68) has proposed a two-compartment equilibrium-kinetic model for describing the solute uptake or release by a sediment. This model is based on the assumption that two types of sorption sites exist: labile sites, S_L, which are in equilibrium with bulk aqueous solution, and hindered sites, S_H, which are controlled by a slow first-order rate process. Conceptually, sorption according to this model can be considered either as a two-stage process:

$$C \underset{K_{eq}}{\rightleftharpoons} q_\ell \overset{k_{12}}{\underset{k_{21}}{\rightleftharpoons}} q_h \qquad (35)$$

or, alternatively, as a parallel process:

$$q_\ell \underset{K_{eq}}{\rightleftharpoons} C \overset{k_{12}}{\underset{k_{21}}{\rightleftharpoons}} q_h \qquad (36)$$

where C is the solution concentration and q represents the sorbed concentration. Karickhoff and Morris (68) observed that the fraction of labile sites decreased with increasing sorption and, more importantly, the rate of desorption was inversely proportional to K_{ow}.

The two-phase kinetic model developed by Karickhoff (65) is capable of fitting either the sorption or desorption of a sorbing solute. For linear isotherms, the mathematical description given by Karickhoff (1) and others (67, 70, 71) is virtually identical to that of a mass transfer process (72).

We may also postulate that the rate of sorption or desorption can be described by a diffusive mechanism. The application of diffusion equations to describe the uptake of a sorbing solute can be quite restrictive because of the need to satisfy rigid boundary conditions (68, 73). However, solutions for the diffusive uptake into such different geometries as a plane sheet, a cylinder, or a sphere deviate only slightly (73). Therefore it is useful to examine the solution to the diffusion equation to evaluate important parameters controlling the diffusive uptake of a solute.

The Diffusion Model. The uptake of a solute by a sorbent can be analyzed by a diffusion model, which has been used successfully to model adsorption rates onto activated carbon (74, 75) ion exchangers (72), heterogeneous catalysts (76), and soil columns (77). For the purpose of illustration, we can consider the diffusion of a compound into a spherical sorbent grain under conditions of linear sorption and no exterior mass transfer limitations (73), which is described by

$$\frac{\partial C}{\partial t} = \frac{D_e}{1 + R_p}\left(\frac{\partial^2 C}{\partial r^2} + \frac{2}{r}\frac{\partial C}{\partial r}\right) \qquad (37)$$

where D_e = effective diffusion coefficient, (L^2/T); R_p = a dimensionless equilibrium partition coefficient, r = radial distance from the center of the sorbing grain, (L), and t = time. R_p is a dimensionless partition coefficient equal to $\rho/\varepsilon K_d$, where ρ = sorbent grain density (M/L^3), ε = sorbent internal porosity (L^3/L^3), K_d = sorbent partition coefficient (L^3/M). The effective diffusion coefficient accounts for the molecular diffusivity and tortuosity in the sorbent grain.

When the sorbent is initially free from solute, Equation 37 can be solved analytically (73) to give the ratio of the mass sorbed at time t to the mass sorbed at equilibrium (i.e., the fractional approach to equilibrium). The mathematical solution depends on the mass fraction ultimately sorbed from the aqueous phase (F), and is most conveniently presented in terms of τ, a dimensionless time parameter given by

$$\tau = \frac{1}{1 + R_p}\frac{D_e t}{a^2} \qquad (38)$$

where a is the radius of the sorbent grain. The quantity $[a^2(1 + R_p)]/D_e$ can be considered a relaxation time for diffusion accompanied by linear sorption. Three solutions to Equation 38 corresponding to values of F equal to 0.2, 0.5, and 0.8 are illustrated in Figure 7.

Several important assumptions were necessary to achieve the solution given in Equation 38. First, it is assumed that the rate of sorption is much faster than the rate of diffusion. This implies that all solute in the internal pores of the sorbent is at equilibrium with its immediate surroundings. In addition, it is assumed that the sorption sites are homogeneous and that once a compound is sorbed to the solid, it does not migrate along the surface. Finally, to solve the diffusion equation, the inherent assumption required is that the geometry or physical dimensions of the sorbent do not change during the course of the experiment due to abrasion, dissolution, swelling, or other process.

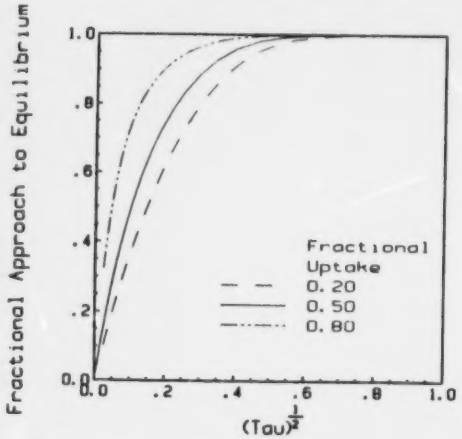

Figure 7. The fractional approach to equilibrium (after 73). Fractional uptake = mass of solute sorbed at equilibrium/mass of solute added to system; fractional approach to equilibrium = mass of solute sorbed at time τ/mass of solute sorbed at time ∞.

Figure 7 shows that for F = 0.5, a sorbing (or desorbing) solute will have reached 95% of the ultimate sorption capacity at $(\tau_{95})^{1/2} = 0.38$. If we assume $R_p \gg 1$, then Equation 38 can be rearranged to give

$$t_{95\%} = \frac{(0.38)^2 R_p a^2}{D_e} \qquad (39)$$

Thus we see that $t_{95\%}$ is proportional to R_p and square of particle radius.

For a hypothetical sorbent with properties listed in Table II, we assume that experiments have shown that sorption of dichlorobenzene (log K_{ow} = 3.3) is 95% complete within one day. R_p equals 1000 on the basis of the correlation of Karickhoff et al. (15). If we estimate R_p for other solutes from the same correlation and assume negligible mineral sorption, we may estimate the time required to reach 95% of equilibrium for other compounds. These calculations imply that approximately 0.1 days will be required to reach 95% equilibrium for benzene (log K_{ow} = 2.1), approximately 10 days for 1,2,4,5-tetrachlorobenzene (log K_{ow} = 4.7) and approximately 100 days will be required for hexachlorobenzene (log K_{ow} = 5.5). Clearly the time required to approach equilibrium can be substantially longer than provided in usual laboratory protocols, depending on the strength of sorption.

Table II. Assumed Sorbent Properties Used to Estimate the Time to Equilibrium

Property	Assumed Value
Bulk density (ρ)	1700 (kg/m^3)
Internal porosity (ϵ)	0.05 (-)
f_{oc}	0.02 (-)
Molecular diffusivity (D_{mol})	10^{-9} (m^2/s)
Tortuosity (T)	10
Particle radius (a)	2.4×10^{-4} m

Since the same general solution holds for desorption under conditions of linear equilibrium, similar arguments can be employed to describe the diffusion out of the sorbent (73).

Previously, it was noted that organic matter associated with the coarse fraction of a sorbent was a substantially weaker sorbent than the organic matter associated with smaller materials (15). This discrepancy is consistent with a radial diffusion model: since $\tau_{95\%}$ is proportional to a^2 (Equation 39), the time required to reach equilibrium should increase with the square of the particle diameter. Clearly if the same mixing time were used for both fine-grained and coarse-grained sorbents, the coarser material could have been far from equilibrium.

Wu and Gschwend (78) successfully employed a radial diffusion model to describe laboratory observed sorption and desorption kinetics. Their data show that sorption and desorption rates were slower for more hydrophobic compounds and sorbents with a larger grain size in a manner consistent with the radial diffusion model.

In many early experiments, hysteresis was observed for highly hydrophobic compounds such as PCBs (79, 80). Since the time to reach equilibrium can be quite long for strongly hydrophobic compounds, a solute may have never reached equilibrium during the sorption isotherm experiment. Consequently, K_d would be underestimated, which leads to the discrepancy between the sorption and desorption coefficients that was attributed to hysteresis. The case for hysteresis being an artifact is supported by recent data for tetrachlorobenzene (log K_{ow} = 4.7), illustrating that sorption and desorption require approximately two days to reach equilibrium with approximately equal time constants (78). Finally, the diffusion model is consistent with the observation that the extent of hysteresis was inversely related to particle size (81).

Summary and Conclusions

In general, the driving force for the sorption of nonpolar organic compounds by sediments is their incompatibility with water as a solvent, i.e., their hydrophobicity, and their affinity for the lipophilic environment of the sediment organic matter. If the fraction of organic matter is low and the specific surface of the mineral matrix is high relative to the hydrophobicity of the solute, sorption by mineral surfaces may become significant, and organic sorption may become insignificant. Practical approaches for evaluating dominance

ranges for organic and inorganic sorptions have been evaluated. If the aqueous phase contains organic cosolvents or organic macromolecules, the aqueous-phase activity of the hydrophobic solute is lowered. The effect of organic macromolecules (usually characterized as DOC) has been modeled as a binding between the hydrophobic solute and the macromolecule. The effect of organic cosolutes has been modeled by semi-empirical correlations. The significance of both effects increases with increasing hydrophobicity of the organic solute and the concentrations of DOC and cosolvents. DOC may be responsible for hysteretic adsorption isotherms in batch adsorption experiments.

The kinetics of sorption can be considered as the sum of two processes: 1) rapid sorption by labile sites which are in equilibrium with solutes dissolved in bulk solution, and 2) hindered sorption by sites which are accessible only by slow diffusion. Alternatively, sorption kinetics can be modeled by a radial diffusional process into spherical sorbents. The slow sorption process prevents complete equilibration within one day, the time used in typical batch experiments. Because the apparent rate of diffusion decreases with increasing hydrophobicity, time to equilibrium is longer for highly hydrophobic compounds.

The description of the sorption process is largely based on empirical correlations, without knowledge of the detailed structure of the sediments. No doubt, in the future a greater effort will have to be made to understand sorption behavior in terms of sediment constituents. It will not suffice to consider sorption onto sediments simply in terms of partitioning into a uniform, thermodynamically ideal, stationary organic phase.

List of Symbols and Abbreviations

Symbols:

a	radius of a sorbent grain (L)
C	aqueous concentration (ML^{-3})
C_b	aqueous concentration for solute bound to dissolved macromolecules (ML^{-3})
C_{doc}	aqueous concentration of dissolved organic carbon (ML^{-3})
C_o	organic-phase concentration of a solute (ML^{-3})
C_w	aqueous concentration of a freely dissolved solute
C_T	$C_b + C_w$ (ML^{-3})
D_e	effective diffusivity (L^2T^{-1})
f	fractional approach to equilibrium (-)
f_{io}	fraction of inorganic material (-)
f_{oc}	fraction of organic carbon (-)
F	fractional uptake (-)
G	Gibbs free energy
HSA	hydrophobic surface area (L^2)
k	Boltzmann constant (JK^{-1})
k_{12}	empirical rate constant (T^{-1})
K	equilibrium constant (varies)
K_d	distribution coefficient (L^3M^{-1})
K_{doc}	distribution coefficient between free and DOC-bound solute (L^3M^{-1})

K_{io}	distribution coefficient for solute bound to inorganic surfaces (L^3M^{-1})
K_{oc}	organic-carbon-normalized distribution coefficient (L^3M^{-1})
K_{ow}	octanol-water partition coefficient (-)
K^e_{oc}	K_{oc} excluding the effect of C_{doc} (L^3M^{-1})
K^e_{ow}	ideal K_{ow} (L^3M^{-1})
K_s	surface specific partition coefficient (L^2M^{-1})
n	porosity (-)
q	sorbed concentration (M/M)
r	radial distance from the center of a sorbing grain (L)
R	gas constant ($JK^{-1}mol^{-1}$)
R_p	equilibrium partition coefficient (-)
S	aqueous solubility (ML^{-3})
S_A	specific surface area (L^2M^{-1})
S_ℓ	aqueous solubility of a supercooled liquid (ML^{-3})
S_m	aqueous solubility in a mixed solvent (ML^{-3})
S_s	aqueous solubility of an organic solid (ML^{-3})
t	time (t)
T	absolute temperature (T)
T_m	melting temperature (T)
V_i	molar volume of solute in phase i (L^3M^{-1})
x	mole fraction concentration ($mol\ mol^{-1}$)

Greek Symbols:

α	empirical constant (-)
γ_i	activity coefficient of a solute in phase i (-)
γ_i	activity coefficient of a solute in phase i saturated with a cosolvent (-)
δ	solubility parameter of a solute ($cal\ M^{-1}L^{-3})^{1/2}$
δ_p	solubility parameter of a polymer ($cal\ M^{-1}L^{-3})^{1/2}$
$\Delta\gamma^c$	difference in surface tension (Mt^{-2})
ϵ	sorbent internal porosity (L^3L^3)
ρ	sorbent grain bulk density (ML^{-3})
ρ_{oc}	bulk density of organic matter (ML^{-3})
τ	time constant for diffusion accompanied by linear sorption (-)
ϕ	volume fraction of solute in polymer (-)
ϕ_p	volume fraction of polymer in solution (-)
χ	Flory-Huggins interaction parameter (-)
χ_H	enthalpic contribution to χ (-)
χ_S	entropic contribution to χ (-)
Ω	efficiency factor for sorption (-)

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Literature Cited

1. Karickhoff, S.W. J. of Hydraulic Engineering 1984, 110, 707-35.
2. Mortland, M.M. Adv. Agron. 1970, 22, 75-114.
3. Mortland, M.M. In "Ground Water Quality"; Ward, C.H.; Giger, W.; McCarty, PL., Eds.; John Wiley & Sons: New York, 1985; pp. 370-86.
4. Healy, T.W. In "Organic Compounds in Aquatic Environments"; Faust, S.J.; Hunter, J.V., Eds.; Marcel Dekker, Inc.: New York, 1971; Chap. 7.
5. Fuerstenau, D.W. In "The Chemistry of Biosurfaces"; Hau, M.L., Ed.; Marcel Dekker, Inc.: New York, 1971; Vol. 1, Chap. 4.
6. March, J.W. "Advanced Organic Chemistry"; John Wiley & Sons: New York, 1985; p. 73.
7. Franks, F. In "Water: A Comprehensive Treatise"; Franks, F., Ed.; Plenum Press: New York, 1975; Vol. 4, p. 4.
8. Cowan, C.T.; White, D. Trans. Fard. Soc. 1958, 54, 691-7.
9. Leo, A.; Hansch, C.; Elkins, D. Chem. Rev. 1971, 71, 525-616.
10. Tanford, C. "The Hydrophobic Effect"; 2nd ed.; Wiley-Interscience: New York, 1980; p. 14.
11. Hansch, C.; Leo, A. "Substituent Constants for Correlation Analysis in Chemistry and Biology"; Wiley Interscience: New York, 1979.
12. Hamaker, J.W.; Thompson, J.M. In "Organic Chemicals in the Soil Environment"; Goring, C.A.I.; Hamaker, J.W., Eds.; Marcel Dekker, Inc.: New York, 1972.
13. Chiou, C.T.; Shoup, T.D.; Porter, P.E. Org. Geochem. 1985, 8, 9-14.
14. Chiou, C.T.; Peters, L.J.; Freed, V.H. Science 1979, 206, 831-2.
15. Karickhoff, S.W.; Brown, D.S.; Scott, T.A. Water Res. 1979, 13, 241-8.
16. Briggs, G.G. J. Agric. Food Chem. 1981, 29, 1050-9.
17. Reardon, E.J. Groundwater 1981, 19, 279-86.
18. Chiou, C.T. In "Hazard Assessment of Chemicals: Current Developments"; Saxena J.E.; Fisher, F., Eds.; Academic Press: New York, 1981; Vol. 1, Chap. 2.
19. Chiou, C.T.; Schmedding, D.W.; Manes, M. Env. Sci. Technol. 1982, 16, 4-10.
20. Chiou, C.T.; Porter, P.E.; Schmedding, D.W. Env. Sci. Technol. 1983, 17, 227-31.
21. Miller, M.M.; Wasik, S.P.; Huang, G.; Shiu, W.; Mackay, D. Env. Sci. Technol. 1985, 19, 522-9.
22. Karickhoff, S.W. Chemosphere 1981, 10, 833-46.
23. MacKay, D. Env. Sci. Technol. 1977, 11, 1219.
24. Yalkowsky, S.H.; Valvani, S.C. J. Chem. Eng. Data 1979, 24, 127-9.
25. Tewari, Y.B.; Miller, M.M.; Wasile, S.P.; Martine, D.E. J. Chem. Eng. Data 1982, 27, 451-4.
26. Banerjee, S.; Yalkowsky, S.H.; Valvani, S.C. Env. Sci. Technol. 1980, 14, 1227-9.
27. Yalkowsky, S.H.; Valvani, S.C.; Amidon, G.L. J. Pharm. Sci. 1976, 65, 1488-94.

28. Flory, P.J. "Principles of Polymer Chemistry"; Cornell University Press: Ithaca, NY, 1956; Chap. 8.
29. Tanford, C. "Physical Chemistry of Macromolecules"; J. Wiley & Sons: New York, 1961; Chap. 4.
30. Prausnitz, J.M.; Lichtenthaler, R.N.; Azevedo, E.G. "Molecular Thermodynamics of Fluid Phase Equilibria"; Prentice-Hall: Englewood Cliffs, NJ, 1985; pp. 306-16.
31. Freeman, D.H.; Cheung, L.S. Science 1981, 214, 790-2.
32. Weast, R.C. "CRC Handbook of Chemistry and Physics"; CRC Press, Inc.: Boca Raton, FL, 1982; pp. C-732-3.
33. Wershaw, R.L.; Burcan, P.J.; Goldberg, M.C. Env. Sci. Technol. 1969, 3, 271-3.
34. Matsuda, K.; Schnitzer, M. Bull. Environ. Contam. Toxicol. 1971, 6, 200-3.
35. Poirrier, M.A.; Bordelon, B.R.; Laseter, J.L. Env. Sci. Technol. 1972, 6, 1033-5.
36. Boehm, P.D.; Quinn, J.G. Geochim. Cosmochim. Acta 1973, 37 2459-77.
37. Hassett, J.J.; Anderson, M.A. Env. Sci. Technol. 1979, 13, 1526-9.
38. Carlberg, G.E.; K. Martinsen, K. Sci. of Total Environ. 1982, 25, 245-54.
39. Molyneux, P. In "Water: A Comprehensive Treatise"; F. Franks, Ed.; Plenum Press: New York, 1975; Vol. 4, p. 678.
40. Kahn, S.U. In "Dynamics, Exposure and Hazard Assessment of Toxic Chemicals"; Hague, R., Ed.; Ann Arbor Science: Ann Arbor, MI, 1980; pp. 224-9.
41. Chiou, C.T.; Porter, P.E.; Shoup, T.D. Env. Sci. Technol. 1984, 18, 295-7.
42. Carter, C.W.; Suffet, I.H. Env. Sci. Technol. 1982, 16, 735-40.
43. Landrum, P.F.; Nihart, S.R.; Eadie, B.J.; Gardner, W.S. Env. Sci. Technol. 1984, 18, 187-92.
44. Gschwend, P.M.; Wu, S. Env. Sci. Technol. 1985, 19, 90-6.
45. Voice, T.C.; Weber, Jr., W.J. Env. Sci. Technol. 1985, 19, 789-96.
46. Haas, C.N.; Kaplan, B.M. Env. Sci. Technol. 1985, 19, 643-5.
47. Caron, G.; Suffet, I.H.; Belton, T. Chemosphere 1985, 14, 993-1000.
48. MacCarthy, J.F.; Jimenez, B.D. Env. Sci. Technol. 1985, 19, 1072-7.
49. Rao, P.S.C.; Hornsby, A.G.; Kilcrease, D.P.; Nkedi-Kizza, P. J. Environ. Qual. 1985, 14, 376-83.
50. Fu, J.K.; Luthy, R.G. "Pollutant Sorption to Soils and Sediments in Organic/Aqueous Solvent Systems"; EPA/600/3-85/050, 1985.
51. Nkedi-Kizza, P.; Rao, P.S.C.; Hornsby, A.G. Env. Sci. Technol. 1985, 19, 975-9.
52. Curtis, G.P. Engineers Thesis, Stanford University, Stanford, CA, 1984.
53. Nkedi-Kizza, P.; Rao, P.S.C.; Johnson, J.W. J. Environ. Qual. 1983, 12, 195-7.
54. Lambert, S.M. J. Agr. Food Chem. 1968, 16(2), 340-343.
55. McCarty, P.L.; Reinhard, M.; Rittman, B.E. Env. Sci. Technol. 1981, 15, 40-51.

56. Schwarzenbach, R.P.; Westall, J. Env. Sci. Technol. 1981, 15, 1360-7.
57. Shin, V.O.; Chodan, J.J.; Walcott, A.R. J. Agric. Food Chem. 1970, 18, 1129-33.
58. Pierce, R.H., Jr.; Olney, C.E.; Felbeck, Jr., G.T. Geochim. Cosmochim. Acta 1974, 38, 1061-73.
59. Means, J.C.; Wood, S.G.; Hassett, J.J.; Banwart, W.C. Env. Sci. Technol. 1982, 16, 93-8.
60. Kahn, A.; Hassett, J.J.; Banwart, W.L. Soil Sci. 1979, 128, 297-302.
61. Hassett, J.J.; Banwart, W.L.; Wood, S.G.; Means, L.C. Soil Sci. Soc. Am. J. 1981, 45, 38-42.
62. Parris, G.E. Env. Sci. Technol. 1980, 14, 1099-106.
63. Curtis, G.P.; Roberts, P.V.; Reinhard, M. Water Resour. Res. 1986 (in press).
64. Farmer, V.C.; Russell, J.D. Clays Clay Miner. 1967, 15, 121-42.
65. Texter, J.; Klier, K.; Zettlemoyer, A.C. In "Progress in Surface and Membrane Science, Vol. 12"; Academic Press: New York, 1978; p. 339.
66. Karickhoff, S.W. In "Contaminants and Sediments, Vol. 2"; R. Baker, Ed.; Ann Arbor Science: Ann Arbor, MI, 1980.
67. McCall, P.J.; Agin, G.L. Environ. Toxicol. Chem. 1985, 4, 37-44.
68. Karickhoff, S.W.; Morris, K.R. Environ. Toxicol. Chem. 1985, 4, 469-79.
69. Blatt, H.; Middleton, G.; Murray, R. "Origin of Sedimentary Rocks"; Prentice Hall, Inc.: Englewood Cliffs, NJ, 1981; Chap. 13.
70. Hassett, J.P.; Milicic, E. Env. Sci. Technol. 1985, 19, 638-43.
71. Hawker, D.W.; Connell, D.W. Env. Sci. Technol. 1985, 19, 643-6.
72. Helfferich, F. "Ion Exchange"; McGraw-Hill Book Co.: New York, 1962; pp. 259-62.
73. Crank, J. "The Mathematics of Diffusion"; Oxford University Press: Ely House, London, 1975; Chaps. 6, 14.
74. Weber, W.J. Jr.; Rumer, R.R. Water Resour. Res. 1965, 1, 361-9.
75. Weber, T.W.; Chakravorti, R.K. AIChE J. 1974, 20, 228-38.
76. Satterfield, C.N. "Mass Transfer in Heterogeneous Catalysis"; MIT Press: Cambridge, MA, 1970; Chap. 1.
77. Rao, P.S.C.; Davidson, J.M.; Jessup, R.E.; Selim, M.M. Soil Sci. Soc. Am. J. 1979, 43, 22-8.
78. Wu, S.; Gschwend, P. Submitted to Env. Sci. Technol. 1986.
79. DiToro, D.M.; Horzempa, L.M. Env. Sci. Technol. 1982, 16(9), 594-602.
80. Horzempa, L.M., DiToro, D.M. Water Res. 1983, 17(8), 851-9.
81. Rao, P.S.C.; Berkheiser, V.E.; Ou, L.T. "Estimation parameters for modeling behavior of selected pesticides and orthophosphate"; EPA-6001, U.S. Environmental Protection Agency, Athens, GA, 1984.

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